The Tracer Study of the Reactions of Diphenyl Sulfone and Diphenyl Sulfoxide with Sulfur

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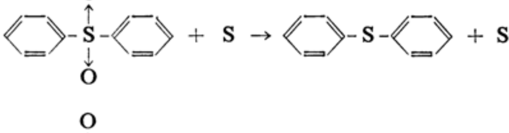
Many years ago, Krafft and Vorster[1] obtained diphenyl sulfide and sulfur dioxide (Eq. 1) when they heated diphenyl sulfone with sulfur in nitrogen atmosphere. They also performed many other thermal reactions between organic sulfur compounds and sulfur or selenium. Among their observations an especially interesting reaction is that between diphenyl sulfone and selenium as expressed by Eq. 2, because the displacement of SO_2 group in the sulfone with elemental selenium may imply that a similar replacement of sulfur atom of diphenyl sulfone with elemental sulfur is taking place in the reaction.



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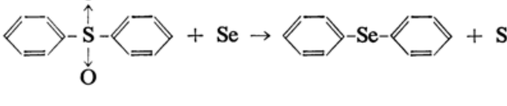

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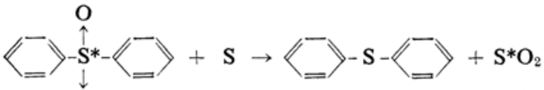
[1] F. Krafft and Vorster, *Ber.*, 26, 2813 (1893).

TABLE I. REACTIONS OF ORGANIC SULFUR COMPOUNDS WITH SULFUR

	Original	Sulfide (after converted to sulfone)	Reduction	Replacement	Conditions	Yield
	c.p.m./mg.	c.p.m./mg.	%	%		%
Diphenyl sulfone	2520	673	26.7	73.3	304°C*(30 min.)	80
	2520	641	25.4	74.6	394°C (15 min.)	
Diphenyl sulfoxide	3776	3548	94.0	6.0	280°C (30 min.)	93

* Air-bath temperature



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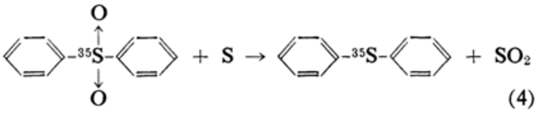
Years later, Böeseken[2] extended this reaction to p,p'-halogeno and p-bromo-p'-methyl derivatives of diphenyl sulfone but found that they react in entirely different manners; namely, the former gave dihalogen substituted products of benzene and sulfur dioxide and the latter only hydrogen sulfide. However, all the past observations seem to indicate that once C-S bond cleavage takes place, SO_2 group of the sulfone leaves off quite readily. In the case of p,p'-halogenated diphenyl sulfones, halogeno-phenyl radical formed in the sulfur-induced cleavage perhaps easily abstracts halogen from other molecule.

It is known that the force constant of S-O bond in sulfone calculated from infrared data, 9.5×10^5 dyn./cm.[3a], is appreciably higher than that of sulfoxide (7×10^5 dyn./cm.)[3a], therefore, unlike those in sulfoxide groups, the sulfur-oxygen links in sulfone groups are not easily cleaved[3b]. In this thermal reaction between diphenyl sulfone and sulfur, it is not unreasonable to consider that SO_2 group in the sulfone may be replaced by sulfur with no cleavage of S-O bonds, while the S-O link in the sulfoxide would be merely reduced with sulfur to sulfide, although the latter reaction has never been reported.

We have investigated the mechanism of these reactions by examining the accompanying exchange of sulfur atom in the reaction of sulfur-35 labeled diphenyl sulfone with ordinary sulfur. Diphenyl sulfide-^{35}S was prepared by Friedel-Crafts reaction of benzene with radioactive sulfur and was converted to the sulfone by oxidation with potassium permanganate. This diphenyl sulfone-^{35}S was treated with ordinary sulfur. The reaction was rather sluggish below 300°C but proceeded nicely at above 300°C giving diphenyl sulfide over 80% yield. The sulfide thus obtained was reoxidized back to the sulfone whose specific activity was compared with that of the original sulfone. These results are tabulated in Table I. Inspection of the data suggests that one-fourth of the over-all reaction proceeded by apparent reduction and the other three-fourths underwent by replacement as one could foresee from the reaction of diphenyl sulfone with selenium.

If one assumes that the over-all reaction is consisted with two simultaneous reactions, i. e., reduction and replacement, and that the reactions have different energies of activation, then one would expect that the ratio of two reactions may change at different temperatures. However, if the two reactions have similar temperature factors, the ratio would remain the same. When the reaction was performed nearly at the boiling temperature of sulfone, 379°C, however, no apparent difference was observed.

In the meantime the over-all reaction could be considered as a combination of two successive reactions, i. e., the initial reduction and the following sulfur exchange reaction between the sulfide and remaining sulfur as shown below:



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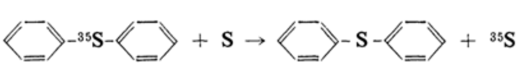

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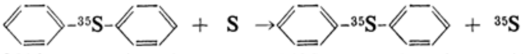
Incidentally we found that this type of exchange (Eq. 5) actually occured when diphenyl sulfide-^{35}S was refluxed for two hours at 313°C together with natural sulfur.



2520 c.p.m./mg.* 1425 c.p.m./mg.* (56.5%) (6)

* Converted to the sulfone

Supposing the exchange rate is much faster than the reduction rate, the amount of radioactivity remained in the sulfide at the end of the reaction will be shown by the following simple equation (see appendix);

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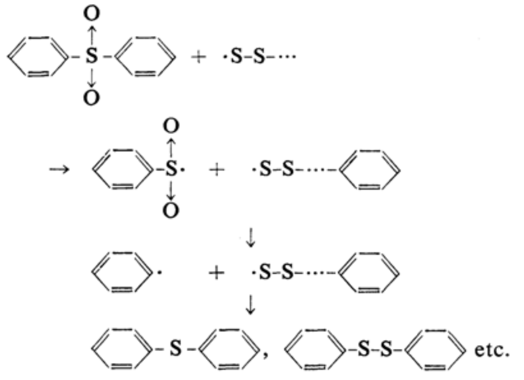
[2] J. Böeseken, *Rec. trav. chim.*, 30, 137 (1911).

[3a] These values are of alkyl sulfoxides and sulfones, C. C. Price and S. Oae, "Sulfur Bonding", Ronald Press, Inc., New York (1962), p. 66; 3b) ibid., p. 132.

$$\frac{y}{a}=1-\frac{1}{e}=0.632 \tag{7}$$

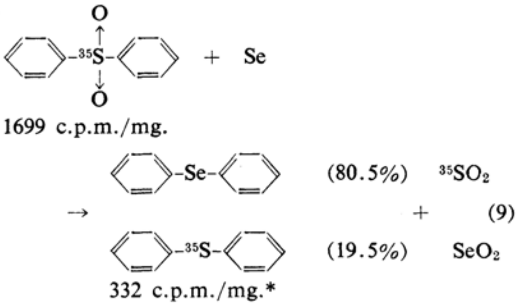
where a is the specific activity of the sulfone used and y is the specific activity of the sulfide formed. This indicates that the exchange will transport only 36.8% in total activity from the sulfide to sulfur and major portion of activity, i. e., 63.2% will remain in the sulfide. Therefore, this mechanism also cannot explain the radiochemical results.

The most likely pathway for the main reaction will be the initial cleavage of C–S bond of the sulfone, followed by the formation of diphenyl sulfide, a part of which further undergoes sulfur exchange. It is known that sulfur behaves as biradical chain at high temperature4) and diphenyl sulfide was obtained together with by-products such as hydrogen sulfide, diphenyl disulfide, etc. when a mixture of benzene and sulfur was heated at 350°C5). We also found that a little amount of diphenyl disulfide and polymer-like substance formed in the reaction of diphenyl sulfone with sulfur (Eq. 1). From these facts, it is quite certain that the C–S bond of the sulfone cleaves first, induced by the biradical chain of sulfur, then sulfur dioxide leaves off and the sulfide and a small portion of the disulfide forms in the main reaction. As to the apparent reduction which amounts to about 25%, there are two possibilities, the one is a straight forward reduction that takes place simultaneously with the replacement and the other is the sulfur-exchange reaction between sulfur and diphenyl sulfide. In view of the small percentage, 6%, of replacement reaction in the case of diphenyl sulfoxide, major portion of the apparent reduction reaction of the sulfone would be the real reduction and only several percentage of the apparent reduction originate from the exchange between sulfide formed by the initial replacement and the remaining sulfur.



(8)

If the reduction takes place in parallel with the replacement, the sulfide must be formed in the reaction of diphenyl sulfone with selenium, too. In this reaction, however, diphenyl sulfide cannot be separated easily from diphenyl selenide because both the sulfur and the selenium compounds display quite similar chemical properties. To overcome this difficulty, diphenyl sulfone-^{35}S was reacted with selenium for 1 hr. at 305°C and it was found that about one-fifth of the activity of the original diphenyl sulfone-^{35}S remained in the reaction product, apparently the mixture of diphenyl selenide and sulfide. This means that the reduction indeed occured (Eq. 9).



(9)

* Converted to the sulfone and selenone

It is interesting to note that benzene or biphenyl was not found among the reaction products of the reaction between diphenyl sulfone and sulfur and biphenyl was not found in the direct reaction of benzene with sulfur5), while the reaction of p,p'-dihalogeno diphenyl sulfone with sulfur did not give dihalogeno diphenyl sulfide, but did give dihalogeno benzene2). We can not offer any satisfactory explanation, however, most of phenyl radicals formed are perhaps immediately caught by sulfur chain before they recombine or abstract hydrogen in the former reaction, while halogen-substituted phenyl radicals easily abstract chlorine in the latter.

Meanwhile we found that diphenyl sulfoxide reacted readily with sulfur at lower temperature than the sulfone giving diphenyl sulfide in quantitative yield if mechanical loss was considered. A similar tracer technique was applied in this reaction, too. Diphenyl sulfoxide-^{35}S was used in this reaction which was prepared by oxidation of diphenyl sulfide-^{35}S with an equivalent amount of hydrogen peroxide and this ^{35}S-labeled sulfoxide was treated with ordinary sulfur. The reaction proceeded quite readily at around 280°C and diphenyl sulfide was obtained in nearly quantitative yield. The sulfide thus obtained was converted

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4) W. A. Pryor, "Mechanisms of Sulfur Reactions", McGraw-Hill Book Co., Inc., New York (1962), p. 8.

5) H. B. Glass and E. E. Reid, *J. Am. Chem. Soc.*, **51**, 3428 (1929).

to diphenyl sulfone whose activity was counted. The fact that most of the activity in the original sulfoxide remained in the sulfide formed (as shown in Table I) suggests that simple reduction of sulfoxide to sulfide with elemental sulfur took place by the abstraction of labile oxygen atom with sulfur and only a small portion of the reaction proceeded by replacement contrary to the reaction of the sulfone. This is a clear cut reduction. Similar oxygen-transfer reactions from sulfoxides to divalent sulfur compounds are known. For example, thiacyclopentane-1-oxide was reacted with dibenzyl sulfide in acetic acid to give some dibenzyl sulfoxide6), and alkyl sulfoxide is known to form when dimethyl sulfoxide and alkyl sulfide are mixed and heated at 160～175°C7).

A small portion of the apparent replacement reaction can be interpreted either as resulted from the direct exchange between diphenyl sulfide formed and ordinary sulfur during the reaction or as the initial induced cleavage of the C–S link of the sulfoxide followed by the cleavage of S–O bond and the attack of sulfur chain, as in the case of the sulfone. At present, we have very little knowledge to select one from the other.

Experimental

Diphenyl Sulfide-^{35}S was prepared by Friedel-Crafts reaction addopted by Dougherty and Hammond8). Diluted and recrystallized active sulfur was added to anhydrous aluminum chloride suspended in refluxing benzene and diphenyl sulfide separated was distilled twice, obtaining oil of b. p. 115°C/2.5 mmHg.

Diphenyl Sulfoxide-^{35}S.—To the solution of 7.7 g. of diphenyl sulfide-^{35}S dissolved in glacial acetic acid containing several drops of concentrated sulfuric acid, was added an equimolar amount of 30% hydrogen peroxide slowly with cooling and stirring. Stirring was continued at room temperature for one hour and then the reaction mixture was kept at 50°C overnight. After a large amount of water added, oil separated was crystallized by adding a small piece of crystalline sulfoxide. White hard crystals was recrystallized from benzene-ligroin, obtaining 4.8 g. (57%) of the sulfoxide, m. p. 69～71°C.

Diphenyl Sulfone-^{35}S was prepared by oxidizing diphenyl sulfide-^{35}S with 1.8 times in mole of potassium permanganate in glacial acetic acid containing a few drops of concentrated sulfuric acid with cooling and stirring. After the addition was over it was warmed at 50°C for 30 min., and then an excess of potassium permanganate was reduced by bubbling sulfur dioxide through the solution. The solution was then poured into a large amount of water, and the precipitate formed was recrystallized from benzene-ligroin, yielding brilliant white crystals, m. p. 122～123.5°C, in 44%.

The Reactions of Diphenyl Sulfone with Sulfur.—Diphenyl sulfone-^{35}S (2520 c.p.m./mg.), 0.01 mol., was thoroughly mixed with 0.01 g. atom of natural sulfur in a Claisen-flask and was put quickly in a pre-heated air-bath, passing nitrogen gas through the reaction flask. Reaction started at about 300°C (air-bath temperature) and sulfur dioxide evolved was trapped in a few traps cooled with dry-ice-acetone. After 15 min. when gas evolution ceased, bath temperature was kept at around 304°C for 15 min. and then diphenyl sulfide was distilled slowly by elevating bath temperatue. When diphenyl sulfide came out, there remained a small amount of sludge insoluble in most organic solvents and water. Crude diphenyl sulfide obtained was redistilled once more, and crystals remained in the distilling flask, m. p. 59°C was found to have the same melting point with diphenyl sulfide when it was mixed with the authentic sample. Diphenyl sulfide was repeatedly distilled untill it became transparent, usually two to three times, then was converted to diphenyl sulfone using the previous method (673 c.p.m./mg.). By the same way as above diphenyl sulfone-^{35}S was treated at 394°C (air-bath temperature), and the activity for the final sulfone was found to be 641 c.p.m./mg.

The Exchange Reaction of Diphenyl Sulfide-^{35}S and Sulfur.—A mixture of diphenyl sulfide-^{35}S (2520 c.p.m./mg. converted to the sulfone), 2.32 g. and 0.39 g. of sulfur was refluxed for 2 hr. at 313°C in nitrogen atmosphere. The sulfide was recovered by distillation. Light yellow oil was redistilled once and converted into sulfone to be subjected to counting analysis (1425 c.p.m./mg.).

The Reaction of Diphenyl Sulfone-^{35}S and Selenium.—Colloidal red selenium was freshly prepared by bubbling sulfur dioxide through the water solution of selenium oxide. Diphenyl sulfone-^{35}S (1699 c.p.m./mg.) and selenium, 0.01 g. atom, respectively, was thoroughly mixed and heated in nitrogen atmosphere. Gas evolved from air-bath temperature of 288°C for 30 min. Bath temperature was kept at 304～306°C for additional 30 min. and then distilled. The oil obtained was redistilled three times, b. p. 300°C, 0.59 g. This oil was oxidized using the previous method. An excess of potassium permanganate was reduced with sulfur dioxide with cooling and it was poured into a large amount of water before oily selenide came out by reduction with excess of sulfur dioxide. After recrystallization from benzene-ligroin, m. p. 135～136°C, 0.3 g. (332 c.p.m./mg.) was obtained.

The Reaction of Diphenyl Sulfoxide with Sulfur.—Diphenyl sulfoxide-^{35}S (3776 c.p.m./mg. converted to the sulfone), 0.01 mol., was mixed with 0.005 g. atom of natural sulfur in a Claisen-flask and treated by the same way as in the reaction of the sulfone. Sulfur dioxide evolved at 280°C (air-bath temperature). The sulfide obtained in quantitative yield was converted to the sulfone (3548 c.p.m./mg.).

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6) F. G. Bordwell and B. M. Pitt, ibid., **77**, 572 (1955).

7) S. Searles, Jr. and H. R. Hays, *J. Org. Chem.*, **23**, 2028 (1958).

8) G. Dougherty and P. D. Hammond, *J. Am. Chem. Soc.*, **57**, 117 (1935).

Counting Analysis. — All the compounds was converted into the sulfone or selenone and was counted by Packard, Tri-Carb, liquid scintillation counter, in toluene solution using POPOP as scintilator.

Summary

Diphenyl sulfoxide-^{35}S was reduced to the sulfide-^{35}S nearly quantitatively by heating with sulfur at 280°C, while diphenyl sulfone did not react with sulfur at the same temperature. At around 300°C, diphenyl sulfone-^{35}S started to react with sulfur and gave diphenyl sulfide that lost nearly 75% of the original activity of ^{35}S of the sulfone used. The main reaction of the sulfone was found not to be reduction, but substitution involving induced C–S cleavage and replacement with sulfur chain.

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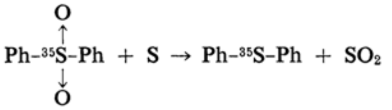
Appendix

For convenience in the discussion, the following mechanism and conditions (a—c) will be assumed in the reaction shown below, Eqs. 1 and 2.



$$\mathrm{Ph}\text{-}{}^{35}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-}\mathrm{Ph} + \mathrm{S} \rightarrow \mathrm{Ph}\text{-}{}^{35}\mathrm{S}\text{-}\mathrm{Ph} + \mathrm{SO_2} \qquad (1)$$

$$\mathrm{Ph}\text{-}{}^{35}\mathrm{S}\text{-}\mathrm{Ph} + \mathrm{S} \rightarrow \mathrm{Ph}\text{-}\mathrm{S}\text{-}\mathrm{Ph} + {}^{35}\mathrm{S} \qquad (2)$$

a) There is no exchange of sulfur atom between diphenyl sulfone and the sulfide or between the sulfone and sulfur.

b) The rate of sulfur exchange shown by Eq. 2 is much faster than the rate of reduction, i. e. Eq. 1.

c) Sulfur dioxide formed will escape from the system so rapidly that there is no time for sulfur dioxide to participate in sulfur-exchange reaction.

Here, let us define x as an amount (in mole) of diphenyl sulfone undergone to the sulfide, y, the specific activity (c.p.m./mol.) of the sulfide when x mol. of the sulfone is converted into the sulfide, v, total amount (in mole) of the sulfone used which is equal to total amount of sulfur or total amount of the sulfide formed in the reaction and a, the specific activity of the sulfone (c.p.m./mol.).

When $(x+\mathrm{d}x)$ mol. of the sulfone is converted to the sulfide, the total activity of the resulting sulfide will be $(xy+a\mathrm{d}x)$; therefore the specific activity will be expressed by $(xy+a\mathrm{d}x)/(x+\mathrm{d}x)$. Meanwhile, the total activity of sulfur at that time will be $[v-(x+\mathrm{d}x)]y$. After an rapid equilibrium is attained between the sulfide and sulfur by exchange, the specific activity will become

$$\frac{[v-(x+\mathrm{d}x)]y+xy+a\mathrm{d}x}{v}$$

Therefore the small variation of specific activity, $\mathrm{d}y$ can be expressed as,

$$\mathrm{d}y=\frac{[v-(x+\mathrm{d}x)]y+xy+a\mathrm{d}x}{v}-y$$

$$=(a-y)\frac{\mathrm{d}x}{v}$$

Integrating this equation, one can get

$$\ln\frac{a}{a-y}=\frac{x}{v}$$

When the reaction is completed, x becomes equal to v; therefore the above equation gives

$$y=a-\frac{a}{e}$$

The ratio of the specific activity of the sulfone and that of the sulfide, y/a, will then be

$$\frac{y}{a}=1-\frac{1}{e}=0.632.$$